Characterization of minor adducts formed *in vitro* by reaction of 2'-deoxyguanosine with 2-acetoxyamino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP).

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PhIP minor adduct products, as well as previously-characterized dG-C8-PhIP, were identified from the reaction of *N*-acetoxy-PhIP with 2'-deoxyguanosine (dG). Nucleosidic adducts were characterized by UV/vis, fluorescence, mass spectrometry, and in some cases proton NMR spectroscopy. Reaction of *N*-acetoxy-PhIP with dG yielded primarily dG-C8-PhIP (~ 80 - 90 %, $(M+H)^+$ = 490 Da) and at least four additional adducts, three with $(M+H)^+$ = 508 Da and a fourth with $(M+H)^+$ = 490 Da. Results from collisional dissociation of these molecular ions confirmed PhIP-related adducts; two $(M+H)^+$ = 508 Da adducts were putatively assigned as hydrolyzed, ring-opened N7 adduct isomers, and the other $(M+H)^+$ = 490 Da species was putatively assigned as an adduct to the exocyclic amine position of guanine. Incubation of dG-C8-PhIP under alkaline conditions (pH 12.5) indicated oxidation, yielding the spirobisguanidino-PhIP nucleoside adduct [$(M+H)^+$ = 506 Da] plus 2-guanidino-PhIP, neither of which was produced in the reaction of dG with *N*-acetoxy-PhIP. Finally, ^{32}P-postlabeling data suggested that some or all of the minor PhIP adducts are formed to DNA *in vivo*, although their significance is as yet unknown. *Work performed under auspices of U.S.D.O.E. by LLNL, contract W-7405-ENG-48, and supported by NIH (CA55861) and USAMRDC (MM4559FLB).*